The University of Chicago
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CAMBRO-SILURIAN LIMONITE ORES OF PENNSYLVANIA

A DISSERTATION SUBMITTED TO THE FACULTIES OF THE GRADUATE SCHOOLS OF ARTS, LITERATURE, AND SCIENCE, IN CANDIDACY FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

(DEPARTMENT OF GEOLOGY)

BY
THOMAS CRAMER HOPKINS

CHICAGO, ILLINOIS
1900

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FIGURE 1.—SAMPLES OF LIMONITE ORE

Numbers 1–5, bombshell ore; 6–11, pipe ore; 12, brecciated ore

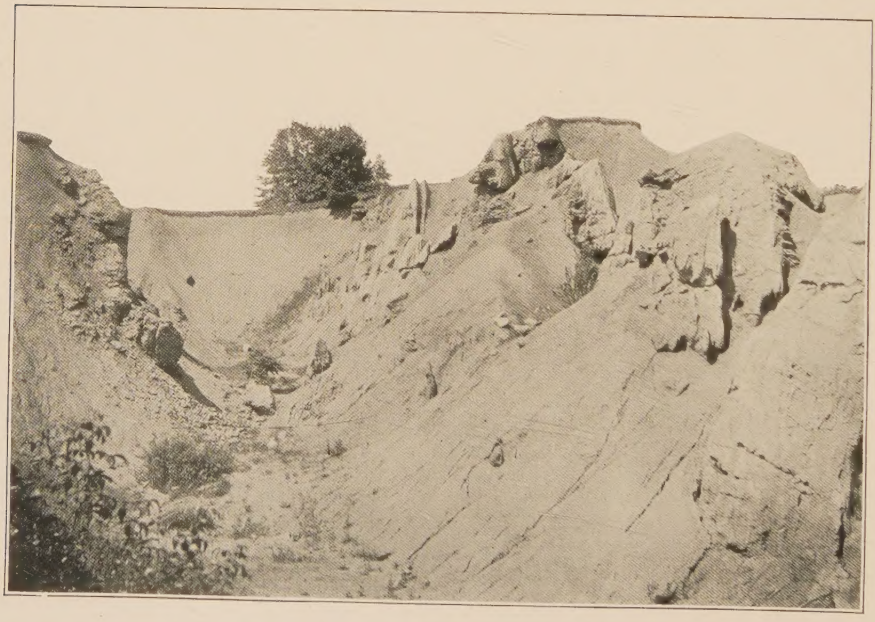

FIGURE 2.—VIEW IN THE HUNTER ORE BANK

Showing an ore pocket in eroded cavity in the limestone

CAMBRO-SILURIAN LIMONITE ORES OF PENNSYLVANIA*

BY T. C. HOPKINS

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Introduction

The object of this paper is to explain the genesis of the limonite ores of the limestone valleys in central and eastern Pennsylvania, to show the original sources of the iron, the modes of its accumulation, and to account for its frequent occurrence along with more or less extensive bodies of white and parti-colored clays. The data and conclusions presented are based on field studies of the limonite ores of the limestone areas in the Great valley and in portions of Nittany valley.

The occurrence of limonite ores in Pennsylvania has been known a great many years; in fact, they have been employed in the manufacture of iron ever since that industry began in this country. They occur in

*This paper has been accepted for publication in the Bulletin of the Geological Society of America, volume 11.

every geological formation and in every county in the state, but this paper treats only of those in the limestone valleys of the central and eastern portions and the closely associated ores of the underlying slates. What is said will apply equally well to many similar deposits along the Great valley of the Appalachians, but it is not intended primarily to include all of the Great valley deposits, or any part of them outside of Pennsylvania.

Much has been written about these limonite deposits, and many explanations have been offered to account for them. While the different hypotheses heretofore advanced have been taken into consideration, the conclusions in this paper are, as previously stated, based primarily on field observations made by the writer during the years 1898 and 1899.

Geological Position of the Ores

The limonite ores in question occur in residual deposits on the Ordovician and Cambrian limestones and slates. They are referred to in literature as the Cambro-Silurian ores, signifying that they occur partly in the Cambrian and partly in the Silurian rocks, but that portion of what was formerly called Silurian is now more commonly called Ordovician. The Ordovician portion of the series is included in the number II or Trenton group of the classification of the Second Pennsylvania Geological Survey. Trenton, as thus used, includes all the Ordovician below the Utica shale. The lower portion of the series, including the slates and quartzites, is called group number 1 or "Chiques quartzite" by the Pennsylvania Survey. In the earlier reports it was correlated with the Potsdam of New York, but Lesley in his later reports advised the use of the local term, Chiques or Hellam. Walcott's more recent investigations* show that the quartzite, slates, and some of the limestones carry the Olenellus fauna, and hence are Lower Cambrian. The Upper and Middle Cambrian faunas have not been determined in this area, except the lower horizon of the Middle Cambrian in one locality. The upper portion of the limestones carries the Trenton fauna, and a few Chazy and Calciferous forms have been found in lower portions, but the strata between the Trenton at the top and the Lower Cambrian have so far shown no well defined fauna, and have not been carefully classified. It has not been possible even to draw a definite boundary between the Cambrian and the Ordovician, so we are compelled to still speak of the strata in their entirety as Cambro-Ordovician. It is on them that the ores in question occur, some near the top of the Trenton, some on the Lower Cambrian, and many over the vague horizons between these limits.

* Bull. No. 134 of the U. S. Geol. Survey.

It should be noted, however, that the ore deposits in large measure are on and not in the rocks of this age—that is, they are residual deposits and have been formed since the uplift of these beds in late or post-Permian time. The process of formation is going on at present and has been presumably more or less continuous since Carboniferous time.

Description of the Ores

Associated minerals and classification

The bulk of the ores consists of the mineral limonite, associated with which are variable quantities of the other hydrous oxides, turgite and goethite, and the anhydrous oxides, hematite and magnetite.*

The ores occur in many diversified forms, which might be variously classified, but for convenience the following group names, based on form, are used by the author: nodular ore, pipe ore, brecciated ore, flake or sheet ore, fragmental ore, and yellow ocher.

Nodular ore

The nodular ore consists of irregularly rounded masses, varying in size from a fraction of a pound to several hundred pounds in weight. The masses are frequently hollow (see numbers 2 and 3 in figure 1 of plate), but some inclose a rounded or subangular rock fragment (see number 1 in figure 1), which is sometimes sandstone, as in the illustration, sometimes chert, sometimes slate, and sometimes clay. Some of the shells are filled with clay or sand, and workmen report finding many of them filled with water. Some are filled with clay, which still retains the laminated structure and appearance of the original slate from which the clay was derived. Furthermore, this slaty structure was found to extend through the ore shell, which showed, besides the plain lamination of the slate, a faint concentric structure as well. This shell, which is illustrated in figure 1, was not found imbedded in the slate, but in the loose material on an outcrop of it where it occurred along with many similar ones. It was clearly a concretionary form in the slates, an advanced stage of the concentric structure that may be seen in almost any shale bed. While only one shell was found still retaining the laminations in the clay, there were many others containing clay and sand. Some of the shells are but thin crusts, while others are quite thick, almost solid; some have a rough irregular inner surface, while others have a smooth, velvety or bright mammillated inner surface, frequently

*The extensive deposit of magnetite at Cornwall, Pennsylvania, while occurring at about the same geological horizon, is so intimately associated with igneous dikes that it will not be considered with the limonite deposits.

coated with manganese oxide. In some instances the lining of the shell is covered with a great many small stalactites of ore, indicating a deposit on the interior since the shell was formed. Many of the shells are lined with a dense fibrous layer, often an inch or more in thickness. The last two varieties resemble some of the quartz geodes and indicate a similar origin. The thinner shells have nearly all been broken, and we see only the fragments of them in the clay-ore masses. This shell form of the ore is common throughout the area and forms an appreciable part of the ore body in many places. The small, irregular, nodular-like pieces of ore, commonly known as shot ore, are presumably closely related in origin to the shells, the difference being that the segregation was around more numerous centers, and hence resulted in smaller pieces.

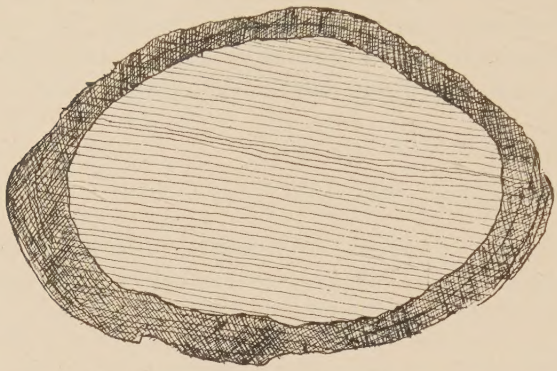

FIGURE 1.—*Cross-section of Ore Nodule from Cambrian Slates.*

PIPE ORE

Pipe ore comprises two distinct types, one of which (illustrated by numbers 6, 7, 8, 9, and 11 in figure 1 of plate) consists of heavy compact pipe-like masses from 1 or 2 to 8 or 10 inches in diameter, the ore crust being from a fraction of an inch to 3 inches or more in thickness. In nearly all cases this type of pipe ore is impregnated with clay, grains of sand, and other foreign material. The inference is that the iron oxide was deposited around lime stalactites or stalagmites which were subsequently leached out and carried away. The presence of the sand and foreign material in the oxide suggests that the lime stalactites were imbedded in the clay and sand when the deposition of the iron took place. The other type of the pipe ores consists of a loose aggregation of slender pipes or rods, all having a general parallelism and each pipe cemented to its neighbors at frequent intervals. The iron oxide is comparatively free from impregnating foreign material. Somewhat similar forms of lime carbonate have been observed where the waters from a lime spring trickle over an overhanging, jagged ledge of rock, either on the surface or in a subterranean cavity, and the inference is that the pipe ores have been formed in a somewhat similar manner. They have all been broken

from their original position, and are now found only in fragments intermingled in the clay mass. The pipe ores have not been observed in the sandstone or slate areas, but are abundant in limestone ore regions, in some places forming the major part of the ore.

BRECCIATED ORE

The brecciated ore consists of fragments of chert, sandstone, or slate, cemented by iron oxide into a solid mass. These masses are sometimes quite large, many tons in weight, forming so-called solid ore bodies. Frequently the inclosed rock fragments disintegrate and crumble out, leaving the more or less cavernous skeleton of ore (see number 12 in figure 1 of plate). Brecciated ore is found on the limestones, on the clay, and on the sand deposits. It occurs in large quantities on the sand deposits in the Nittany valley, where the greater part of the inclosed fragments consists of chert from the overlying limestones. I have nowhere observed any limestone fragments in any of the brecciated masses. It is possible that some of the hollow spaces may represent former limestone fragments which have all been leached out. The brecciated ores are most abundant where the ore masses rest on the sandstone or intercalated clay beds, and while in general they are most abundant near the bottom of the deposit, huge blocks of them are scattered at various levels through the clay-ore mass.

FLAKE OR SHEET ORE

Flake or sheet ore occurs in the joint and bedding seams of the limestone and slates. So far as it has been observed *in situ* it occurs in comparatively thin flaky laminated sheets, often less than an inch in thickness (see numbers 2 and 4 in figure 1 of plate). As the surrounding rock is leached away, the ore sheets and flakes are carried down and more or less broken up and mingled with the other materials. The nature of the ore fragments observed in the residual clay shows this type of ore to be locally the most abundant of all those mentioned, while in other localities it is almost entirely wanting.

FRAGMENTAL ORE

Fragmental ore consists of irregular angular fragments of all sizes commingled with the residual clay, being probably in all cases broken remnants of the preceding forms. It is not always possible, however, to refer the fragment to its original form, as there is often no essential difference in appearance between a small fragment of a sheet and that of a pipe or a shell. In several localities, most noticeably in the limestone districts, there are rounded water-worn fragments of the ore asso-

ciated with partly rounded chert and sandstone pieces. These are local in occurrence and form a comparatively small part of the ore deposits. They may be caused in part by surface and in part by subterranean streams. An especially favorable point for them is at the bottom of a sink-hole, where the surface waters pouring in during the wet seasons wear the materials at the bottom like the pebbles in a brook. The subsequent decay of the limestone buries the rounded materials in the residual clay and obscures the manner of their formation. These sink-holes are quite abundant at the present time, and in the few places where the bottom is accessible the rounded fragments of ore and chert are quite numerous.

YELLOW OCHER

Yellow ocher, while not properly an iron ore, is probably the most common form of the iron oxide in the region considered. It is associated with the ores in all the deposits, and in many places occurs free from lump ore. It represents the diffused iron oxide which has not been segregated. In several places it is prepared for market as ocher, but generally no attempt has been made to save it.

Chemical Composition

The following analyses of carefully selected samples show the chemical nature of the ores. Commercial analyses of carload lots give a much lower per cent of iron and a corresponding increase of silica and alumina, as shown in analysis number 8 of the table, which gives the average of 29 analyses, each of which represents 150 to 500 specimens of ore. The commercial analyses include considerable mechanical impurities in the form of clay and sand that were eliminated as far as possible in the other analyses. Doctor Genth, who made most of the analyses, says the ores are mechanical mixtures of limonite with hydrous ferric silicate and minute traces of hydrous ferric phosphate. It is impossible, he says, to state whether the hydrous ferric silicate is anthosiderite or degeroite, or, he might have added, one or more of several other hydrous ferric silicates, of which chloropal is a common form. There is a possibility also that some of it may occur as grünerite or some other iron, or iron-magnesian, amphibole, or pyroxene. Bischof* says that hydrate of iron will decompose silicate of alumina. The deposition of the ores in contact with the clays and cherts would furnish opportunity for such chemical reaction. That the waters carrying the iron have a chemical action on the silica is shown by the dissolution of the chert, shale, and sandstone fragments inclosed in the shells and the breccias.

* Elements of Chemical and Physical Geology, vol. 2.

Analyses of selected Specimens of Limonites

	1. Pipe ore, Hostler bank.	2. Pipe ore, Pennsylvania bank.	3. Pipe ore, Hunter bank.	4. Pure fibrous, Dry Hollow bank.	5. Pure fibrous, Bull bank.	6. Amorphous compact brown ore, Lytle bank.	7. Clean dark brown ore, Centre county.	8. Average of 29 commercial analyses.
Fe_2O_3	78.58	83.74	78.57	83.13	81.48	82.00	68.26	62.11
MnO_2	.08	.31	.01	.15	.07	Tr.	.19	2.85
Al_2O_3	.88	.33	1.21	.74	.49	1.94	.28	2.39
MgO	.54	.34	.55	.09	Tr.	.17	.08	.42
CaO	.30	Tr.	.62	Tr.	Tr.	Tr.	.07	.48
P_2O_5	.36	.14	.36	.50	.08	.37	.96	1.10
SiO_2	4.25	2.57	7.65*	2.47	3.98	2.98	16.13*	18.97
Quartz	2.60	.44	.....	.....	.....	.44	.....	.....
H_2O	12.41	12.13	11.16	12.92	13.00	12.10	12.24	11.62
S	.....	.....	.028	.....	.....	.....	.011	.06
Total	100.00	100.00	100.19	100.00	100.00	100.00	98.22	100.00

Numbers 1, 2, 4, 5, and 6 analyzed by F. A. Genth.
Number 3 by A. S. McCreath.
Number 7 by John I. Thompson, Lemont, Pennsylvania.

Some of the dissolved silica may enter into chemical combination with the iron; some of it may simply be carried down with the iron in minute particles. The deposition of the iron in the presence of minute particles of clay might inclose some of the particles without any chemical action and the association be so close and the included particles so minute that they could not be separated by any mechanical means. The phosphorus may occur in combination with the iron as vivianite, triplite, or some of the associated forms, or perhaps as a basic ferric phosphate, or it may be in combination with the alumina. Evidence favoring the latter supposition is the prevalence of wavellite, which occurs in large quantities closely associated with the ores in several localities (see page 9), and the occurrence of ceruleolactite in the ore mine in Chester valley.

The phosphorus will probably form a hydrous phosphate, whether it combines with the iron or the alumina. The remaining alumina probably is in combination with silica and water. This will not leave sufficient water to form limonite with all the iron, in the molecular ratio commonly given, namely, $2Fe_2O_3$, $3H_2O$. In fact, if all the water com-

*Insoluble residue. The analysis of the insoluble residue in number 7 gave: SiO_2 = 13,505 Al_2O_3 2.4, CaO .078, MgO .147.

bines with the iron, it is not sufficient to form the theoretical limonite. Hence we must assume either that the water and iron combine in a different ratio and form a new compound or, what is more probable, that there is a mixture of the limonite and one of the other hydrous oxides.

I have computed the hypothetical combinations of the elements given in analysis number 1 on two bases, first assuming that the phosphorus combines with the alumina to form wavellite, and, secondly, that it combines with iron to form vivianite, and the silica combines with iron to form grünerite. If one of the hydrous ferric silicates is formed, the proportions would be changed slightly, as shown in a third combination. After forming the wavellite, the remaining alumina is put in the form of kaolin, and the remaining water and iron are combined so as to form all the limonite possible, and the iron in excess is put into the goethite, the next highest oxide.

1.		2.	
	Per cent.		*Per cent.*
Limonite, $2Fe_2O_3, 3H_2O$	77.79	Limonite	75.65
Goethite, Fe_2O_3, H_2O	8.07	Goethite	9.61
Grünerite, $FeSiO_3$	8.40	Grünerite	8.59
Wavellite	.78	Vivianite	1.95
Kaolin	1.30	Kaolin	8.70

The small per cent of manganese is supposed to be in the form of the oxide. The lime and magnesia are presumably in the form of the carbonate.

Hypothetical Combinations of the Elements in the Limonite Ores

Computing the excess Silica as Anthosiderite

	No. 5. Bull bank.	No. 1. Hostler bank.	No. 2. Pennsylvania bank.	No. 6. Lytle bank.
Limonite	92.80	65.72	54.23	44.51
Goethite		23.49	39.95	44.70
Anthosiderite, $2Fe_2O_3, 9SiO_2 2H_2O$	5.91	4.05	4.06	2.39
Wavellite	.39	.993	.45	.76
Kaolin	.77	1.29	.26	3.61
Quartz		2.60	.44	.44
$Fe_2O_3 : H_2O$ (molecular)	496 : 747 2 : 3 nearly limonite.	478 : 652 3 : 4 nearly.	515 : 660 4 : 5 nearly.	506 : 625 4 : 5 nearly.

Computing the excess Silica as Chloropal.

Limonite	63.60	34.78	36.85	33.66
Goethite	26.52	50.73	59.10	57.85
Chloropal, Fe_2O_3, $3SiO_2 5H_2O$	8.60	8.62	5.92	3.01
Wavellite	.39	.99	.45	.76
Kaolin	.77	1.29	.26	3.61
Quartz		2.60	.44	.44
$Fe_2O_3 : H_2O$ (molecular)	489 : 660 3 : 4 nearly.	471 : 564 4 : 5 nearly.	510 : 599 5 : 6 nearly.	505 : 595 5 : 6 nearly.

If the silica is combined with the iron in the form of anthosiderite, it will be seen that the remaining iron and water in number 5 will be in the proper ratio to form limonite, and hence this seems a probable combination; but in numbers 1, 2, and 6 the iron and water are in the proportion of 3 : 4 and 4 : 5. If chloropal is formed, the iron-water ratio is 3 to 4, 4 to 5, and 5 to 6. It is possible that iron and water may combine in these variable ratios; but until it can be proven in some way, it seems better to consider them as forming mixtures of the established compounds, limonite and goethite or turgite.

Chloropal has been found associated with the iron ores in at least one locality in Lehigh county, and it is likewise a better known mineral than anthosiderite, and in this respect its occurrence is more probable.

Associated Minerals

Besides the iron oxides already mentioned, namely, limonite, goethite, turgite, hematite, and magnetite, the other iron minerals present in the ore deposits are ilmenite, siderite, and iron pyrite.* Manganese is associated with the iron ores in many places, and in several different localities the manganese oxides, psilomelane, and pyrolusite have been mined and shipped. The analyses show the presence of manganese in all the ores.

Wavellite occurs associated with the iron ores in several localities, and in one place near Mount Holly Springs it is found in commercial quantities. At Glen Loch the wavellite occurs in crystal forms in the old iron ore pit. Quartz crystals are found in a few localities, while chert and hornstone are quite common. Fluorite has been observed in at least three localities, and the quite rare mineral ceruleolactite occurs at the Glen Loch ore mines, in the Little Chester valley.

Associated Rocks

In the valley regions the prevailing rock is limestone, which varies in composition from nearly pure carbonate to a form with a high percent-

*Second Pennsylvania Geol. Survey, D, p. 26.

age of silica, and from dolomite to a variety nearly free from magnesia. In Nittany valley, in Center county, the upper portion of the limestone is highly calcareous, while the lower portion is very arenaceous, in fact grading in several places into a silicious sandstone, which reaches a thickness of 300 or 400 feet.

White Clay

Intercalated with both the Ordovician and the Cambrian limestones and associated with the Cambrian quartzites underneath the limestones are beds of hydromica slates, which on exposure weather into clays. These clays are frequently parti-colored from the iron oxide stains, but in many localities are almost entirely free from iron and are nearly snow white. These white and parti-colored clays are very intimately associated with the iron ores, in a great many banks the ores resting on or against a deposit of the clay.

Exposures of the white clay are most numerous in the South Mountain area, in Cumberland county, where it occurs in nearly every one of the ore pits designated on figure 5. Similar deposits occur at various horizons in the limestone valleys, but most abundantly near the base of the Cambrian portion of the limestones. In Lehigh and Berks counties there are several ore pits exposing white clay in the limestones near the top of the Trenton, not far from the contact with the overlying shales. In Nittany valley the clays occur in the proximity of the sandstone beds in what probably corresponds to the Calciferous division, as Calciferous fossils were found in what is to all appearances the same horizon.

The evidence that the white clays are the weathered products of the hydromica slates is (1) the intimate gradation of the clay into the slightly weathered slates, which is shown clearly in clay pits at Latimore, York county, and in the ore pit at Hensingerville (see figure 4); (2) the occurrence in the clay of several ore pits of fragments of the undecomposed slate, and (3) the occurrence in many of the clay exposures of numerous fragments of white quartzite, similar in appearance to the interlaminated thin quartzite lenses which are nearly always present in the slate exposures.

In the Lower Cambrian horizon below the limestones are beds of sandstones, quartzites, conglomerates, and talcose slates. There are many diabase dikes cutting through the sedimentary rocks in different localities, but they bear no direct relation to the ore deposits.

Mode of Occurrence

The ores occur for the most part in fragments of varying sizes, commingled with the residual material resting upon limestones, slates, or

sandstones. The residual material consists of clay, sand, and chert, with occasional fragments of sandstone, limestone, and shale. The relative proportion of the ore to the residual material is quite variable, in most of the pits a good average being one part of ore by bulk to five of residue. Locally the yield may reach 75 per cent or more. In very few localities can the ore be handled with profit if it forms less than 15 per cent of the entire mass. The diffused iron oxide is almost universally distributed through the residuary mass over all the limestone areas, portions only of the white clay deposits being free from it. Isolated ore fragments are pretty widely met, only comparatively small areas being entirely free from them; but areas in which the ore fragments occur in commercial quantities (that is, forming 15 per cent or more of the mass), while numerous, are limited in extent and form a very small proportion of the entire limestone and slate belt. A few of the largest ore banks, such as

FIGURE 2.—*Section at Pennsylvania Furnace Ore Bank.*

Showing occurrence of ore in the bedding and joint seams of the limestone.

the Scotia bank in the Nittany valley, extend over an area of 100 acres or more; but many are limited to less than half an acre, and some are only a few yards in extent.

In the limestone areas the ores occur generally in pockets or solution cavities in the limestone, which are quite irregular in outline and quite variable in depth (see figure 2 in plate, and also text figure 2). The atmospheric waters have attacked the basset edges of the limestones, which have yielded much more rapidly in some places than in others. The clay, chert, sand, and iron oxide—the insoluble materials—collect in these solution cavities. In a few places the ore may be seen in position in the seams of the limestone, one of the best illustrations of which is in the Pennsylvania Furnace ore bank, in the Nittany valley (see figure 2), where it occurs in both the bedding and the joint seams, but most abundantly in the latter, which may be due in part to the fact that they are better exposed to view than the others. The ore deposit is on

the argillaceous and silicious matter in the seam, and not in direct contact with the limestone, which is a sandy, silicious variety, leaving on the weathered surface, in places, a silicious skeleton or framework sometimes coated with ore. The ore is laminated parallel with the walls of the seams. As the limestone decays, the thin sheets of ore break down and mingle with the residual clay, furnishing the commercial ores. The ore which occurs in place in the seams in the limestone and the fragments visible in the residual clay are all thin and fragile so far as observed; but the bottoms of the ore pockets are concealed by debris, and it is possible that the sheets become thicker at greater depths, as is frequently reported by the workmen.

In the slate areas the ore with the other residua rests upon a mass of clay, in many cases white clay, stained locally by iron oxides. As the slates from which the clays are derived are interstratified with the limestones, there can be no very sharp distinction drawn between the ore deposits on the limestone and those on the clay. In many districts the greater part of the ore deposits are found on the white clay. So common is this occurrence that it may be stated as a general rule that in areas where the clays occur they are associated with the ore deposits, but where the clays are absent the ores occur in the eroded cavities in the limestone, as described above. One general distinction can be made between the purely limestone deposits and the limestone-clay deposits. The latter are generally richer at the bottom in direct contact with the white clay, while the former may be as rich at the top as at the bottom. Solid bodies of ore are spoken of by the miners in many places, but I have never seen any such more than a few hundred pounds in weight that were not mixed with foreign materials. Professor Prime, who examined many of the Lehigh Valley mines when they were in operation, says:* "At times a thick, solid bank of ore is found in a mine. This is, however, rare, and continues but a short distance." Lesley† mentions the occurrence of such bodies, but his statements appear to be based on reports by mine superintendents, rather than on his own observations.

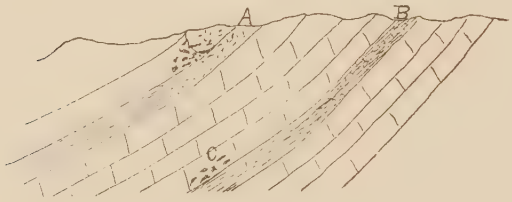

FIGURE 3.—*Ideal Section Illustrating Possible Mode of Accumulating Iron Ore underneath the Clay by Process of Segregation and Leaching.*

Occasionally ore bodies are found in or underneath the white clay.

*Second Geol. Survey of Pennsylvania, Report D D, p. 50.

†Proc. Am. Phil. Soc., vol. xiv.

This may be caused by a segregation of the ores in underlying limestones, and the subsequent leaching out of the intervening rock permits the upper clay to rest on the ore, as shown in figure 3. Should the second accumulation rest on clay the final result is an ore body inclosed in the clay. In some instances the cause of the ore being beneath the clay is an overturn or an overthrust of the strata. Structural relations support this view at several localities on Mountain creek, in Cumberland county. Sometimes it is simply irregularity in weathering.

While usually the ore deposits rest on the white clay, occasionally they occur in it, and in one place, Hensingerville, the ore is found impregnating the hydromica slates from which the clays are derived, thus showing how the ore may get into the clay. In the joint and lamination seams of the slates the ore occurs in thin flakes, which resemble those mentioned in the limestone at Pennsylvania Furnace, except that

FIGURE 4.—*Cross-section of Ore Bank at Hensingerville, Pennsylvania.*

Illustrating accumulations of ore in the hydromica slates.

they are smaller and more numerous, just as the seams of the slate are more numerous and closer together. The exposure is on the south wall of an old ore pit (see figure 4), and the interlamination of the ore extends at least to the depth of the pit, 60 feet below the surface, and presumably deeper, as the pit opening, extending more than 100 feet north, was formed by the removal of the clay for the ore contained therein, and which must in part, at least, have come from slates underlying those exposed. When the workmen making the excavation came in contact with the but partially disintegrated slates on the south face, the mining was no longer profitable and operations ceased. A shaft 50 feet back from the quarry face shows a similar occurrence of the ore flakes in the seams of the slate to the bottom of the shaft, 15 feet below the surface. In this mine the bombshell or nodular ore was quite abundant, forming concentric shells in the slate and the resultant clay (see figure 1).

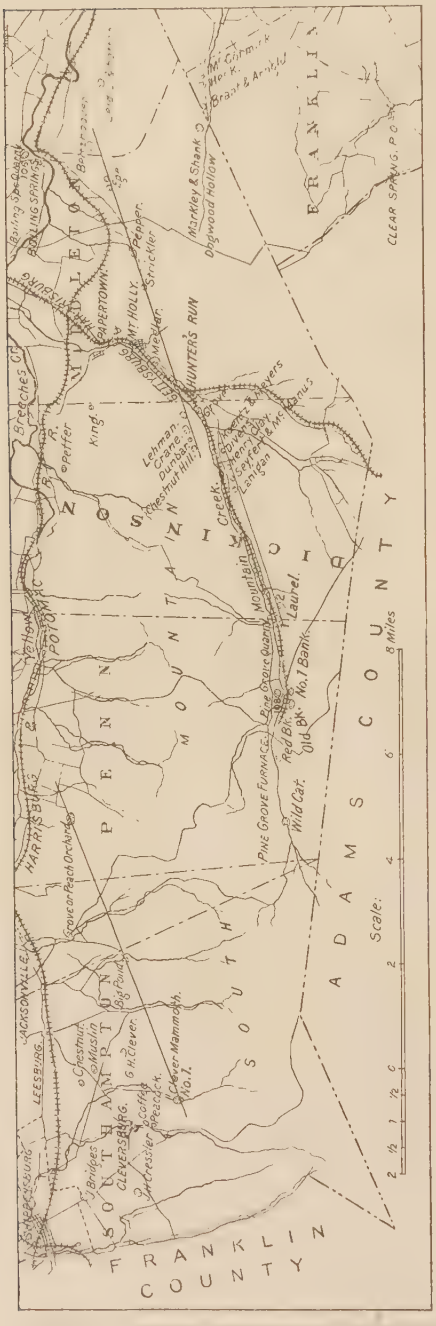

FIGURE 5.—*Map of South Mountain Region, Cumberland County, Pennsylvania.*
Showing the alignment of many of the ore banks.

Some of the ore pits are shallow, striking the limestone *in situ* at a depth of 8 or 10 feet. Many of them range in depth from 50 to 90 feet, but the ore frequently extends to a much greater depth. The expense of elevating the materials and of keeping out the water generally causes a cessation of work at about 90 feet below the surface. The actual depth of the ore deposit in a few places is surprisingly great. At the Lehman mine, in Cumberland county, a hole was drilled 435 feet below the bottom of the ore pit. The report of the boring gave 340 feet of ore (presumably ore and clay), 40 feet of blue clay, 30 feet of white clay, and 25 feet of "mountain clay."* A record of a well-boring at Lambourne, in the Nittany valley, gives 300 feet of ore and clay, 450 feet of white sand, 16 feet of limestone, a total depth of 766 feet, or 750 feet to the solid limestone rock, yet limestone may be seen outcropping on all sides of this well less than half a mile distant. It is difficult to account for the excessive deep disintegration of the rocks at this point.

Prime and Lesley emphasize the statement that the ore occurs in regular belts

*Second Geol. Survey of Pennsylvania, An. Rept., 1886, pt. iv, p. 1462.

along definite horizons. Rogers* says the occurrence of the ores is empirical, and bears no very close relation to the underlying rocks, except in the Kishacoquillas valley, where he finds that the ores occur over the anticlinal axes in the fissures produced by the flexure of the limestones. The parallelism is shown to the best advantage where the slate belts are most pronounced, as the slate or its residual clay determines the location of the ore bodies. The accompanying map of the South Mountain area in Cumberland county illustrates this feature to better advantage than any other area; yet, while it may be noticed that most of the pits occur along well defined belts, quite a number can not be so arranged (see figure 5). These pits lie in the slate area, where there is some intercalary limestone, but the main limestone belt of the valley lies north of the area shown on the map. In the limestone valley areas the parallelism is so subordinate that it has little significance, as shown on the accompanying map of a portion of the Lehigh County ore region (see figure 6).

In the Cumberland County region the prospectors recognize the alignment of the ore deposits and take advantage of it in seeking new bodies of ore, but this can not be followed very successfully in the more purely limestone areas.

In portions of Nittany valley a heavy bed of sandstone in the axis of the anticline restricts the ores to a comparatively narrow belt on either side of the sand ridge, and concentrates them to a considerable extent along the contact of the sandstone and limestone, but elsewhere in the valley ore pits have been opened at many different horizons, ranging from the oldest limestones exposed to the overlying Utica shales.

The conclusion of the writer is that the ore deposits may occur at any horizon in the limestones, but since a great many of the larger deposits occur on beds of sand or clay, residual from sandstones and slates, and since these intercalated beds are generally of considerable extent, there is in such places a consequent alignment of the deposits, corresponding to the strike of the rocks and sufficiently pronounced in a region of slate beds to be useful in following up the ore bodies, but in the limestones free from intercalated slates or sandstones there is very little regularity about the occurrence of the ore.

Original Source of the Iron

The discussion of the origin of the limonite ores may be conveniently divided into two heads—the original source of the iron and the mode of its concentration.

*Geology of Pennsylvania, 1858, vol. 1, p. 479.

The possible sources of the iron in the Cambro-Ordovician limonite ores are (1) the Lower Cambrian slates, where it occurs both as pyrite and silicate; (2) the Cambro-Ordovician limestones and included slates, where it exists as diffused carbonate, sulphide, and silicate; (3) the over-

FIGURE 6.—*Map of Portion of Great Valley Region, western Part of Lehigh County, Pennsylvania.* Showing distribution of the limonite ore pits. Reduced from map in Report D D, Second Geological Survey of Pennsylvania.

lying Ordovician and Silurian shales and sandstones, where it occurs as carbonate, sulphide, and hydrous oxide.

It is well known that all strata contain more or less iron, and those in and bordering the limestone valleys of Pennsylvania are no exceptions.

Each of them has furnished a portion of the iron for the ore deposits, but not necessarily all in the same ratio or even in proportion to the amount of iron which they contain. The manner in which erosion removes material has much to do with what becomes of the different constituents. The erosion of sandstones, clays, and slates is largely mechanical, and the included minerals would in large measure be carried away as sediment along with the rock material. Limestone, however, is largely removed in solution, and the insoluble constituents accumulate in the residue. This is one of the reasons why the writer thinks that much of the iron ore of the limestone valleys has been derived from the Cambro-Ordovician limestones on which they occur.

The reasons for attributing the source of some of the iron to the overlying sandstones and slates are (1) that these rocks contain iron and overlie the rocks on which the ores occur; (2) in some places meteoric waters pass through or over these rocks into the limestones, and as the waters contain organic acids, they would naturally dissolve some of the iron; (3) in some places seepage from the shales at the top of the limestone has been observed to be impregnated with iron. The reasons for thinking that this source of supply is not large in comparison with that from the limestones are (1) that the shales and slates are not readily permeable and serve to turn the water from the limestone where topographic conditions make it possible; (2) that in general the most extensive ore deposits are near the base of the limestones; (3) and that the erosion of the shales is largely mechanical and rapid and most of the iron contained in them would be carried away as sediment.

That the iron in the ore deposits on the lower horizons has been derived in part from the Lower Cambrian slates seems probable, in view of the fact that the slates in some places are impregnated with iron pyrites, the weathered surface often showing many minute cubical cavities from which the pyrite has been leached out. The slates intercalated in the limestones are likewise a probable source of iron, as analyses of samples from three different localities show the following percentages of ferric oxide: 0.91, 5.06, and 2.40. There is a possibility, however, that part of the iron in the slates analyzed may have been carried in from the overlying limestone. That all of the iron is not derived from the hydromica slates is evident from the fact that extensive deposits of ore occur in the Ordovician limestones in localities where the slates do not occur, except in horizons below the ore deposits. The slates, as noted elsewhere, occur in the Ordovician limestones in Lehigh county, but they are not present in Nittany valley, except near the base of the series, in the oldest rocks exposed in the valley. Furthermore, where the slates do occur, the ores

are in nearly all cases on top of them and not underneath. Unless we suppose the iron to be carried upward by ascending waters, which is hardly probable, there appears to be no reasonable way in which the ores in the upper horizons could be derived from slates in the lower ones.

The reasons for thinking that the Cambro-Ordovician limestone series is the principal source of the iron in the ore deposits are: (1) the great number of the deposits in the limestone area and their wide distribution over all the different limestone horizons, from the top to the bottom of the series; (2) the intimate commingling of the ores with the residual clay and chert fragments from the dissolution of the limestones; (3) the almost universal occurrence of the deposits on and not under the intercalary beds of clay; (4) the manner of erosion of the limestone, which is wholly by solution, thus offering the most favorable condition for the preservation and the accumulation of the ores; (5) the limestones contain iron—in small quantities, it is true, but I think sufficiently large. The accompanying analyses of limestones from different localities show an average content of one and a quarter per cent of iron carbonate and sulphide. A thickness of 6,000 feet of limestone, which is present in the Nittany valley, would represent 40 feet of iron ore, which is probably in excess of any deposit in the valley. However, this is subject to a number of qualifications which seriously modify any computations in this line.

On the one hand it can not be assumed (*a*) that all the iron in the limestone is changed to ore proper, as often a considerable portion of it remains in the residual clay in the form of yellow ocher, or (*b*) that all the ore remains in the residual material, as part of it, although a comparatively small part, is carried away as sediment in the streams; I say a small part, because the streams in the limestone area are few in number, small in size, and carry very little sediment; (*c*) many of the ore deposits are not at the bottom, but some of them are near the top of the limestone.

On the other hand, it is to be noted (*a*) that the limestones are in nearly all cases highly inclined, sometimes almost vertical, and the thickness of limestone eroded over any given ore deposit may be much greater than that represented by a section normal to the bedding at that point. This is illustrated in figure 7, where *A O* would represent the actual thickness of limestone over the position of the ore deposit *O* in normal position, but *O B* represents the actual thickness eroded in the inclined position. The fact that part of the limestone was probably eroded during the process of folding would not materially alter the result, as the residual materials would not be greatly shifted thereby. (*b*) There would be a lateral as well as a vertical segregation of the iron. It has been stated that the ore

occurs in pockets in eroded depressions in the limestone. These are in many instances at the bottom of former sink-holes at the surface, and, as shown by the present conditions, these sink-holes may collect the drainage from areas many acres in extent. Both the surface and the subterranean drainage would naturally transport the iron both while in solution and later in the lump form toward the sink or cavity. Further evidence in support of this view is the customary mode of occurrence of the ore in the erosion cavities which are separated by more or less barren areas.

While the percentage of iron in the limestone is small, it forms a comparatively high ratio of the insoluble residue, averaging 24 per cent for the whole 16 analyses. Considering the proportional loss of iron to be no greater than that of the other materials, this would apparently furnish a sufficient supply of iron for all the ore deposits.

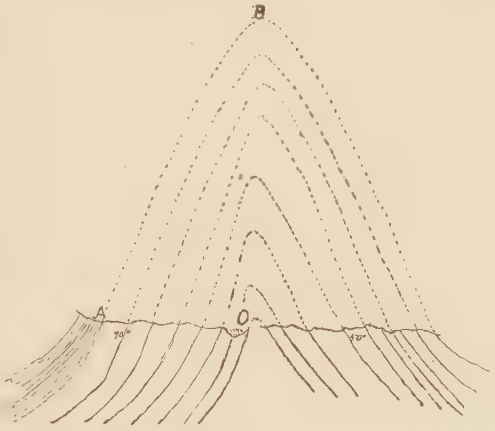

FIGURE 7.—*Cross-section of Anticline in Nittany Valley, Pennsylvania.*

Analyses of the limestones (see page 20) indicate that the iron occurs both as the carbonate and as the sulphide, with the carbonate in excess in all cases. The analyses, while not many in number, are from several quite widely separated localities and presumably represent fairly well the relative amounts of the two compounds, although there may be local enrichments of iron not shown by the analyses. As mentioned under associated minerals, both the carbonate and the pyrite occur in limited quantities in a few places, associated with the limonites, but they are evidently secondary forms, and cannot be considered as indicating in any way the original form of the iron in the limestone. No pyrite crystals have been observed in any of the many limestone exposures examined by the writer. The intercalated hydromica slates in many places contain considerable iron, apparently in the form of silicate, which Bischof states is soluble in carbonate waters, and part of which is presumably added to the supply from the limestone.

The conclusion is that some of the iron in the limonite ore deposits is derived from the overlying Ordovician shales and some from the underlying Cambrian slates, but the chief source is the diffused iron carbonate,

Analyses of Cambro-Ordovician Limestones

	Lehigh county.							Cumberland county.				Franklin county.		Huntingdon county.		
	1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.	12.	13.	14.	15.	16.
$FeCO_3$	1.035	1.450	.538	1.398	1.305	1.188	4.060	.653	1.537	1.552	4.420	.665	1.420	.80	.50	1.31
FeS_2	.030	.611	.268	.105	.320	.238	.174	.076	.186	.102	.011	.011	.....	.....	.....	.....
Insoluble residue	8.980	10.750	8.400	11.670	10.980	7.850	.....	4.040	3.570	5.747	2.310	4.090	2.130	3.84	4.33	18.05
Al_2O_3	.070	.140	.065	.860	.300	.....	6.09	.....	.110	.280	.083	.222	.....	.54	.42	3.81
$CaCO_3$	49.316	51.558	86.036	70.750	56.220	83.632	53.875	57.087	68.225	66.220	72.32	51.743	92.079	59.44	51.82	72.67
$MgCO_3$	40.463	35.216	4.594	15 256	31.201	5.462	25.494	28.314	27.110	26.860	20.590	43.436	4.420	35.19	42.52	3.98
Carbonaceous matter	.250	.210	.420	.120	.120	.835	.....	.130	.010	.050	.....	.....	.....	.....	.....	.....
Phosphorus	.006	.018	.016	.019	.005	.026	.089	.007	.....	.013	.047	.013	.....	.....	.....	.....

Numbers 7 and 16 are from Mineral Resources, U. S. Geological Survey, 1889–1890.
All the others are from Reports M_2 and M_3 of the Second Pennsylvania Geological Survey.
All the analyses except numbers 7 and 16 were made by Doctor Genth.

sulphide, and silicate, mostly the first, in the Ordovician and Cambrian limestones and the intercalated slates.

Mode of Accumulation of the Iron

The form of the ore fragments and the mode of their occurrence, as explained above, necessitate the conclusion that the ores are secondary or derived products. It yet remains to show the manner in which the iron oxide was collected from its diffused condition in the original rock into the deposits of commercial ore in which it now occurs. To bring this about, (1) solution, (2) transportation, and (3) precipitation are necessary. The atmospheric waters are the agents which have produced the change.

Oxygenated waters acting on the pyrite would take it into solution by oxidizing the sulphur into sulphuric acid, part of which combines with the iron as ferrous sulphate and part remains free or combines with any other base that may be present. The reaction is $FeS_2 + 7O + H_2O = FeSO_4 + H_2SO_4$. The H_2SO_4 would readily combine with any lime or magnesia carbonate present, forming the corresponding sulphates. The $FeSO_4$ will rapidly oxidize to basic ferric sulphates and finally to hydroxide.

The iron carbonate is soluble in all acidulated waters—in sulphuric acid as the sulphate, in carbonic acid as the bicarbonate, in organic acids as the corresponding organic salt. As one or more of these acids is nearly always present in meteoric waters near the surface, the solution of any iron carbonate necessarily follows a contact with them. In the presence of oxygen and moisture both the sulphide and carbonate change readily to ferric oxide, which change may take place in the original position of the iron, and later it may be again taken into solution and be added to the iron supply for the ore deposits.

The ferric oxide is much less soluble than the ferrous oxide, and is the most stable form of iron in nature. It is not appreciably soluble in carbonic acid or ordinarily as ferric oxide in the organic acids, although Bischof* and Julien† state that ferric oxide is soluble in apocrenic acid in the presence of ammonia. The organic acids, however, are active reducing agents, and change the ferric oxide to ferrous, in which form it is soluble, as above stated, in any of the acids. Illustrations of this action may be seen at almost any point where roots penetrate yellow clay. A zone of white or light colored clay from which the iron has been leached may be seen surrounding the decayed or decaying roots.

* Elements of Chem. and Phys. Geology.

† Proc. Amer. Assoc. Adv. Sci., 1879, vol. 28, p. 401.

Where there is sufficient vegetable growth, all of the iron may be extracted, as in some of the underclays of the Coal Measures.

The organic acids are an important factor in the transference of the iron, as well as in its solution. In fact, so important and direct is their action that many geologists raise the question whether every great accumulation of iron ore does not necessarily imply the presence of organic matter. The ferrous salts are unstable in the presence of oxygen, and hence would not remain long in solution in meteoric waters unless some reducing agent were present. The organic acids have such a strong affinity for oxygen that as long as they are present they prevent the oxidation of the iron to the insoluble oxide, or, what amounts to the same thing, speedily reduce it to the soluble form again.

The meteoric waters, charged with organic and other acids, reduce, dissolve, and carry away the iron in solution. The next step is its precipitation, which is in most cases from the bicarbonate solution, since carbonic acid is the final stage of all the organic acids. The precipitation may be caused by (1) relief of pressure, (2) oxidation, (3) desiccation or concentration, and (4) neutralization or chemical reaction by another salt in solution, or by replacement of another base in the solid, or it may be a combination of two or more of these causes. The iron may be precipitated as the hydroxide, as the carbonate, or as one of the organic salts, but, in whatever form, it is only a question of time until it is brought to the stable form of the hydroxide. The precipitation from the sulphate solution may be by oxidation alone or, what is more probable, oxidation and neutralization combined.

The precipitation may take place quite remote from the original position or it may be quite near or even at that point, as is the case in the pseudomorphs of limonite after siderite and pyrite. In the limestone regions it is thought that the iron is not carried far in solution, because, as the waters become saturated with lime, which is more soluble than the iron, the latter would be precipitated. A large part of the iron is probably deposited in the upper or cavernous portion of the limestones.

Part of the iron is deposited in cavities and caverns in the limestone, as already indicated in the description of the ore forms. The concentric layers of fibrous ore, lining some of the nodular masses, clearly indicate deposition in a cavity, as do the iron oxide stalactites. The loose masses of pipe ore indicate pretty conclusively that they were formed in caverns, The nodules that were formed by the iron oxide, coating rock fragments. were formed probably in caverns or in the residual material. The brecciated ores were formed by the deposition of the iron in a mass of loose rock material; it may have been in caverns, on the surface, or in the residual material. The sheet ore is, without doubt, formed in seams in

the limestone and in the slate, as already shown (see figures 2 and 4). It is broken up and mixed with the other residua by the leaching away of the surrounding and underlying limestone and by the whole mass sinking down to a lower level. An important horizon for the deposition as well as the accumulation of the ores is at the contact of the limestone with an underlying insoluble layer, such as slate or sandstone.

Some of the ores are oxidized concretionary masses which have formed in the rock before it was disintegrated (see figure 1). I did not see any nodular ore masses in position in the limestones of the area under discussion; but the nodular ore fragments are frequent in the residual material, and they evidently were formed either in the limestones or in the intercalary clay layers.

The accumulation of the clay-ore masses is aided in part by the inequalities in the dissolution of the limestone, and in part by the occurrence of insoluble beds of clay or sand intercalated in the limestones. Thus there is a tendency, in the first place, as previously stated, for the ores to collect in caverns, and as their roofs break through or are dissolved by the waters, there is a further tendency for the loose materials immediately surrounding the cavity to work into it by gravitation, and the ores, being heavier than the clay, tend to work deeper, toward the bottom of the opening.

The interstratified clay and sand beds aid in the concentration of the ores by forming an insoluble layer on which the ores may collect from the overlying limestone. Thus a bed of clay, as shown in figure 3, may serve as a final repository for all the ores of the overlying limestone bed, whether it be 200 or 2,000 feet thick. There will also be a lateral movement down the inclined bed of clay, slate, or sandstone. Thus, in figure 3, for example, all the ore from the triangular space *A C B* may be collected in a comparatively small area at *C*. Should there be a cross-folding in the other direction, at right angles to the main fold, so as to form a synclinal trough down the slope *B C*, the concentration will be all the greater. We have here an explanation of the rich ore deposits on the clay beds in the Great Valley area and on the sand deposits in Nittany valley. It is possible for the concentration to be going on at two or more levels at the same time. Thus in the figure cited the concentration may have begun at *C*, while it is still going on at *A*; but eventually the upper deposit will be brought to the lower one by the leaching out of the intervening limestone. If the clay seam at *A* is comparatively thin, it may lose its identity in the mixture of other materials before reaching the lower level.

If this explanation be the true one, the newest ore, as a rule, will be at the bottom, and the ore deposits will increase in size by additions

below. There is probably no appreciable addition of ore at the top of the mass or any marked enrichment except on the steep slopes, where there is little or no vegetation, and the rivulets wash away part of the imbedding clay into the surface streams.

There is probably to some extent a segregation of the iron oxide into lump ore in the residual material, but I suspect that any such segregation is largely confined to the margin and bottom of the mass, as the body of the clay-ore mass is not readily permeable to water.

The conclusion is that the diffused iron of the limestones and slates is segregated into nodular masses, pipes, and sheets of ore in large measure in the limestone or in the seams and cavities in the same and in or on the top of the slates previous to the final dissolution of these rocks. The leaching away of the limestone leaves the ores scattered through the residual material. The segregating of the oxide may be continued in the residual clays, especially around the margins, but less actively than in the original beds.

Summary

Extensive deposits of limonite ores occur in the residual clays on the Ordovician and Cambrian limestones and slates in the Great valley, Nittany, Kishacoquillas, and Chester valleys, in central and eastern Pennsylvania. The ores are hydrous ferric oxides, consisting largely of limonite, associated with which are local occurrences of turgite and goethite and very limited quantities of hematite, magnetite, pyrite, and siderite. The ores are associated with manganese ores, wavellite, quartz, chert, and fluorite. They occur as pipes, shells, nodular and brecciated masses, and irregular fragments mingled with more or less residual clay and sand lying in irregular pocket-like deposits of varying sizes in cavities on the limestones or on beds of white clay or sandstone.

The original source of the iron is primarily the Cambro-Ordovician limestones and slates, with smaller quantities from the overlying Ordovician and possibly Silurian strata and the underlying slates and quartzites. The iron occurs in these strata as carbonate, sulphide, and silicate, the first being probably the most common.

The segregation of the diffused iron into the ore lumps is brought about by the meteoric waters. The higher oxide is reduced by the organic acids. The ferrous oxide is taken into solution by the organic and carbonic acids, possibly sulphuric acid in some measure. The iron is precipitated from the solution in part as the hydroxide, in part as the carbonate, which is later oxidized. Some of the ores have been concretionary segregations, probably as the carbonate, in the original rock, and

subsequently oxidized in the residual material. Some are formed in seams and cavities on and in the beds of slate, limestone, and sandstone. The deposits increase in size largely by the segregation of the oxide into the scattered nodular and flake-like masses in the underlying limestones, which are subsequently leached out, leaving the ores in residual material similar to that in the overlying clay-ore mass which settles down upon it. The ore nodules and flakes may form at any point in the limestone, but the most favorable horizon for their concentration is at or near the contact of the limestone with an underlying bed of slate or sandstone, which forms a collecting place for the ores. The intercalated slates weather to a white clay, which thus forms the repository for many of the ore masses.

Literature on the Limonite Ores

The following bibliography gives a brief summary of what has been published about the origin of the limonite ores in question. In general, reference is made only to the literature bearing directly on the origin of the limestone valley limonites, but a few specific references on other points are mentioned :*

Benton, E. R.: Tenth Census, volume xv, 1880.

The ores are pseudomorphs after broken limestone by filling the cracks and thickening the films, changing from solid limestone above to irregular shell ore at the bottom.

Bischof, Gustav: Elements of Chemical and Physical Geology, volume 2.

Hydrated oxide of iron decomposes silicate of alumina. From a solution of bicarbonate of iron and bicarbonate of lime a current of atmospheric air causes all the iron to be precipitated as hydrated peroxide before the lime begins to separate.

Dana, James D.: American Journal of Science, third series, 1884, volume 28, page 398.

The limonite ore beds of the eastern United States result from the oxidation *in situ* chiefly of ferriferous limestone. The ferriferous limestones were formed in interior basins or marshes by iron bicarbonate or salt of an organic acid washed down from the land over areas of calcareous deposits. These ore beds, although superficial, can not be said to be modern. They have probably been in progress ever since the land emerged from the ocean.

Davis, O. W., Jr.: The iron ores of Maine, Journal United States Association of Charcoal Iron Workers, 1886, volume 1, page 66.

The ores in the vicinity of Katahdin, Maine, which occur in Silurian clay slates, have been formed by the decomposition and oxidation of pyrites.

*A full bibliography on iron ores is published in Bulletin number x of the Minnesota Geological Survey.

D'Invilliers, E. V.: Second Pennsylvania Geological Survey, Report T, page 136.

The pipe ores are caused by (1) the decomposition of iron pyrite in the limestone ore slate bands, which after oxidation as sulphate filled interstices in the limestone and "changed into peroxide by contact with vegetable matter or other organic substances," or (2) the production of ferrous carbonate by reaction between ferrous sulphate and calcium carbonate and afterward changed to limonite by oxidation and hydration. The wash or lump hematites are wash deposits caught in vast caverns of irregular shape.

Ewing, A. L.: Second Pennsylvania Geological Survey, Report T, page 408.

The original condition was as ferrous salts, in most cases carbonate. It is probable that portions of the iron have been dissolved, transported, deposited, and oxidized during the process of rock decay, yet the facts would indicate that the greater part is due to oxidation *in situ*.

Fontaine, W. M.: Quoted by E. C. Pechin in Proceedings of the Iron and Steel Institute, October, 1890.

The ores are formed by the concentrating action of concretionary forces that have collected the once diffused iron into masses, which have a more or less distinctly concretionary structure, or which form beds of nodular ore or crusts lying in inclosing clay.

Frazer, Perifer, Jr.: Second Pennsylvania Geological Survey, Report C, page 142.

The pyrites of the hydromica slates furnish ferrous sulphate and free sulphuric acid which reacts on the soda in the slates, producing sodium sulphate, which in turn reacts on the lime bicarbonate, giving soda carbonate and lime sulphate. The sodium bicarbonates react on the ferrous and ferric sulphates, forming hydrous oxide from the latter and hydroferrous carbonate from the former, which is farther oxidized to ferric hydrate. This is one of many suggestions.

Harden, J. W.: Transactions of the American Institute of Mining Engineers, 1873, volume 1, page 136.

The ore is the residue of the decomposition of the slates and limestones.

Hunt, T. S.: Second Geological Survey of Pennsylvania, Report E, pages 202–204; Transactions of the American Institute of Mining Engineers, volume xi, page 244.

The ores are formed by the oxidization *in situ* of deposits of carbonate of iron, and in some places pyrite interstratified in the more or less argillaceous slates now changed to clay.

Jackson, R. M. S.: Nittany Valley Iron Ores, 1838–'39.

The ores are deposited *in situ* freed from the limestone during the process of erosion and disintegration.

Julien, A. A.: Proceedings of the American Association for the Advancement of Science, 1879, volume 28, page 401.

Whatever the source of the iron oxide may have been, whether pyrite or other ferruginous minerals, the action of humus acids may be suspected. They probably served for its transport and as the erosive agents in the excavation

of the numerous limestone caverns. If it should be established that the iron was first deposited as carbonate, its solution and decomposition were probably accomplished by these acids previous to its oxidation and hydration.

KENDALL, J. D.: The Iron Ores of Great Britain and Ireland, London, 1893.

The limonite ores are oxidized carbonates which are formed by replacement of limestone. The direct source of the iron may have been the clay deposits, but it originally came from volcanic rocks. In the replacement of limestone by iron carbonate there would be a diminution of volume of about 18 per cent. There would be a corresponding loss of 18 per cent in the change from carbonate to limonite.

KIMBALL, JAMES P.: American Journal of Science, September, 1891, and American Geologist, December, 1891.

The iron in solution replaces the lime carbonate in the limestones and is subsequently oxidized.

LEONHARD, ——: Jahrbuch fur Mineralogie, 1845, page 14.

Describes the formation of ferric hydrate stalactites now going on in a mine near cape Cornwall. Stalactites 18 inches long and an inch in diameter have been formed since the mine was abandoned. It seems probable that these were formed by waters carrying iron carbonate in solution.

LESLEY, J. P.: Proceedings of the American Philosophical Society, volume ix, page 463.

The ore is the residue of the Silurian slates and sandy limestones. The geologist can procure specimens of every stage, from limestone which refused to disintegrate and the iron-lime sandstone with the disintegration and crystallization begun to the perfect ball and pot ore.

Proceedings of the American Philosophical Society, volume xiv, page 19.

The original source of the iron is the limestone, from which it is set free during erosion. Three theories, each applicable to different kinds of ores, are: 1, that part of the ores which occupied caverns, fissures, and sink-holes now lie in pockets; 2, the deposits which show gravel and rolled ore and a commingled mass of ore sand and clay are surface washes; 3, there are interstratified beds of brown hematite still in their original position, descending between layers of sandstone and limestone to undetermined depths.

Final Report of the Second Pennsylvania Geological Survey, page 364.

It is quite possible that all the Great Valley limonites are cavern deposits of very recent date, derived from the decomposition of a series of damourite lime shales belonging to various horizons in the Chazy and Calciferous magnesian limestones.

LYMAN, BENJAMIN SMITH: Proceedings of the American Association for the Advancement of Science, 1867, volume 16, page 115.

The ore was deposited in regular beds at the same time as the other rocks. They have been broken into fragments at their outcrop, and the fragments have accumulated in quantities varying according to the lay of the ground.

MERRILL, F. J. H.: Bulletin of the New York State Museum, volume 4, number 19, page 221.

The existence of the carbonate in the deeper parts of some of the mines and their interstratification with the limestones is suggestive of the origin of the limonites by the decomposition of the ferruginous beds, through oxidation and the agency of carbonated waters.

NEWBERRY, J. S.: Engineering and Mining Journal, 1881, volume 31, page 299.

They are the accumulation of iron carried in the surface drainage, deposited by aeration and oxidation. The iron came from the surface drainage of rock and soil, the decomposition of pyritous rocks, and a residual from ferriferous limestones. The formation has evidently been going on from the Cretaceous age to the present.

PENROSE, R. A. F., JR.: Journal of Geology, 1894, volume ii, page 304.

Many of the iron ore deposits in the Cambrian and Lower Silurian can be clearly shown to be due to a superficial replacement of limestone, or even of more silicious rocks like shales, by iron dissolved from ferruginous rocks in the neighborhood. In such cases the iron in the original rock has been dissolved and carried off in carbonated surface water and reprecipitated in the other rocks, all these stages being directly due to surface influences.

PORTER, JOHN B.: Transactions of the American Institute of Mining Engineers, volume 15, page 177.

The ores are formed from oxidized pyrite, which occurs either in masses or disseminated through the older rocks. The saying, "No ore is under where the water stands" is a key to the great cause in the formation of limonite.

PRIME, F., JR.: American Journal of Science, third series, 1875, volume 9, page 438; Transactions of the American Institute of Mining Engineers, 1875, volume 3, page 410.

The brown hematites were probably formed by the oxidation of iron pyrites, but not *in situ*. It is uncertain whether the pyrite was disseminated through the limestone or whether there was a bed especially rich in pyrite. The oxidation of the pyrite produced protosulphate of iron, which reacts on the limestones and the carbonate of lime and magnesia in the damourite slates, producing iron carbonate, which is deposited, and lime sulphate, which is carried off in solution.

Second Pennsylvania Geological Survey, Report D, pages 53, 59.

The pipe ore has evidently formed by deposition from solution by the oxidation of some ferrous salt, probably the carbonate. "The ore must then have been formed either from the decomposition of ferrous salts *in situ*—that is, ferrous silicates or carbonate—from the solution of the ferrous carbonate in the limestone and its redeposition in the damourite slates or from the same reaction of the ferrous sulphate formed by the oxidation of pyrite." The potash of the damourite slates must have exerted an important agency in the formation of the ores in their present position and condition.

ROGERS, H. W.: Geology of Pennsylvania, 1858, volume i, page 183; volume ii, page 721.

Much of the iron (of the ores of the Primal series) was originally pyrite in minute crystals in certain layers of the slate.